

REPORT DOCUMENTATION PAGE				<i>Form Approved OMB No. 0704-0188</i>	
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1. REPORT DATE (DD-MM-YYYY) 22/02/2011		2. REPORT TYPE Final		3. DATES COVERED (From - To) 01/04/2008-30/11/2010	
4. TITLE AND SUBTITLE Toward the Development of Aluminum Cluster-Containing Materials for Propulsion Applications				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-08-1-0161	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Kit H. Bowen, Jr.				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Johns Hopkins University Baltimore, MD 21218				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 875 North Randolph St. Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-OSR-VA-TR-2012-0244	
12. DISTRIBUTION/AVAILABILITY STATEMENT Public					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Aluminum cluster-containing materials offer several potentially important advantages over current aluminum particle-based propulsion technologies. Both theory and experiments suggest that the preparation of such materials may be feasible. During our recent AFOSR grant, by utilizing anion photoelectron spectroscopic techniques, we have investigated salts composed of alkali cations and multiply-charged aluminum cluster anions, magnesium-aluminum clusters, gold-aluminum clusters, aluminum monovalency in Al ⁷⁻ , aluminum hydride polymer anions, hydrogen atom selectivity in Al ^{13H-} , magic numbers in aluminum hydride anions, and gallium nitride clusters. Nine publications and two PhD theses have also resulted from this work.					
15. SUBJECT TERMS aluminum, photoelectron spectroscopy, negative ions, clusters					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Kit Bowen
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code) 410 516 8425

Final Performance Report

Toward the Development of Aluminum Cluster-Containing Materials for Propulsion Applications

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The objective of our AFOSR program is to work toward the development of aluminum cluster-containing materials for propulsion applications. This constitutes the Final Report for our second cycle of funding under grant award number, FA9550-08-1-0161.

The Problem

Aluminum particles are often ingredients in modern solid fuel propellants, with some compositions containing as much as 22% aluminum in the form of 50-100 μm diameter aluminum particles. Not surprisingly, combustion reactions between these particles and their co-fuel(s) are significantly influenced by particle surface areas and other interfacial effects. Burning rates could presumably be improved by using smaller aluminum particles, but efforts in this direction have been impeded by the strong tendency of very small aluminum particles to oxidize. As a result, nominally pure aluminum particles are typically found to have oxidized to mostly aluminum oxide, i.e., only a small core of unreacted aluminum metal survives within an alumina “overcoat”. Aluminum nanoparticles are incredibly reactive! An ideal aluminum-containing solid fuel would be composed of extremely small, unoxidized aluminum clusters, evenly dispersed amongst its co-fuel molecules, so that the combustion reaction could proceed almost homogeneously rather than heterogeneously. Also, an ideal fuel would have to release substantial amounts of energy and copious quantities of gaseous combustion products.

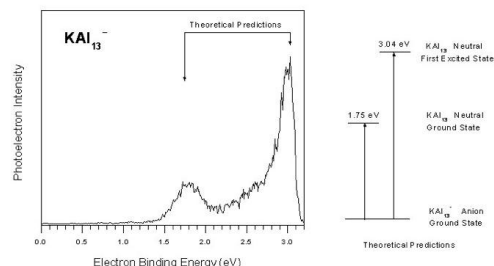
The Solution

To solve this problem, it would be necessary to somehow stabilize aluminum particles within the fuel. For aluminum particles as large as nanoparticles, it may be possible to passivate them with an over-layer of material that prevents their oxidation. But for clusters, with their advantage of ultra-small size and potentially much higher reactivity, stabilization requires their chemical incorporation into the fuel either through ionic or covalent bonding. In the former, an aluminum cluster ion interacts with an ion of opposite polarity to form a salt and ultimately an extended ionic lattice. In the latter, aluminum cluster moieties are covalently bonded to other atoms or ligands. Below, to put our most recent cycle's work in perspective, we first summarize our earlier progress on both the ionic and the covalent sides of this effort. Then, we describe our results from our second (most recent) cycle of funding.

Earlier Progress

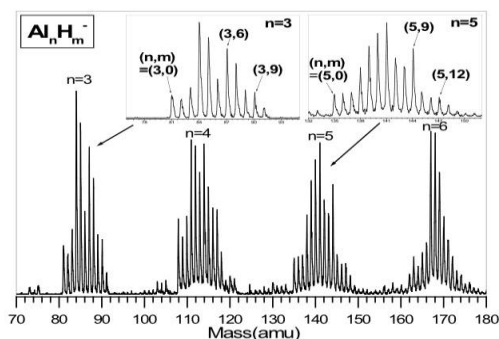
While most aluminum clusters are extraordinarily reactive, there are a few aluminum cluster sizes which are exceptions and which show a significant degree of stability. Of these, the best studied is the “magic cluster”, Al_{13}^- . In terms of size and stability, Al_{13}^- is on a par with the well-known “magic clusters”, fullerenes and metcars. Moreover, Al_{13}^- is highly stable for both electronic and geometric reasons. Electronically, it is a 40 valence electron, closed shell species whose electronic structure is governed by the “shell model”. In this model, the valence electrons are highly delocalized and move under the influence of the smeared-out positive potential of the remaining atomic cations. Geometrically, Al_{13}^- is an icosahedron, with one aluminum atom sitting inside its cage and with the other twelve on its surface. Oxygen etching experiments by Castleman have shown Al_{13}^- to be extraordinarily resistant to oxidation. This is a direct reflection

of its closed shell character and high stability. Also, as shown by Wang, the energy required to remove the excess electron from Al_{13}^- , i.e., the electron affinity of Al_{13} , is the same as that needed to remove the excess electron from Cl^- , i.e., the electron affinity of Cl. For



both Al_{13}^- and Cl^- , this value is 3.6 eV. Since the valence electrons in Al_{13}^- are highly delocalized, one can envision it as a “smooth”, almost spherical object with the same electron binding energy as Cl^- . Under these circumstances, one can perform a Gedanken experiment in which the Cl^- anion in highly ionic KCl, i.e., K^+Cl^- , is replaced by an Al_{13}^- cluster anion to give KAl_{13} , i.e., $\text{K}^+\text{Al}_{13}^-$. The resulting entity can be viewed as an ionic, cluster-assembled, diatomic “molecule”, made-up of a cation and an intact Al_{13}^- anion. This is, in fact, what Khanna, Jena, and Rao did when they conducted calculations on the bonding within KAl_{13} , finding it to have the characteristics of a salt “molecule”. Our own work on this topic was aimed at experimentally testing the theoretical prediction. After developing techniques for generating beams of KAl_n^- anions, we conducted mass-selected, photoelectron spectroscopic studies on it as shown in the accompanying figure, finding good agreement between the transition energies measured in our experiments on KAl_{13}^- and those predicted by theory. Also, experiments by Nakajima on neutral KAl_{13} reached the same conclusion. The viability of this species suggests the possibility that such molecules could form extended ionic lattices.

On the covalent side, we generated about two hundred previously unknown stoichiometries of aluminum hydride



molecules/clusters, Al_nH_m^- and measured the anion photoelectron spectra of many of them. The

truncated mass spectrum presented here, generated while aluminum was being ablated and H_2 was being dissociated in a pulsed arc discharge source (PACIS), shows only a small number of the many new aluminum hydride species formed in this way. DFT calculations were used to simulate the photoelectron spectra of several of these newly discovered aluminum hydride cluster anions and to provide geometric structures for both the anions and their corresponding neutrals. These structures were also found to be consistent with those based on Wade-Mingos electron counting rules. In cooperation with Schnoeckel in Karlsruhe we then synthesized derivatives of these aluminum hydrides, Al_nR_m using his unique co-condensation apparatus. Upon determining their structures by x-ray diffraction, it was seen that they have the same gross structures as the aluminum hydride clusters that we generated in the gas phase. Thus, these clusters/molecules are rare examples of species whose discovery in the gas phase gave impetus to their analogs being synthesized in the condensed phase, where they were isolated and characterized by conventional chemical methods.

Results from our Most Recent Cycle of AFOSR Funding (4/1/08 – 11/30/10)

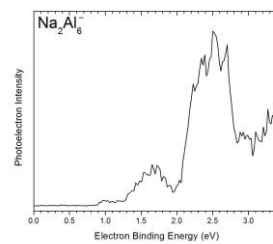
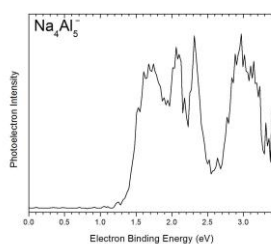
Salts Composed of Alkali Cations and Multiply-Charged Aluminum Cluster Anions

A significant portion of our work has focused on characterizing the electronic properties of neutral, ionic “molecules” (salts) in which their anionic moieties are aluminum clusters. “Molecules” of this type may be building blocks of extended ionic lattices, i.e., of ionic materials. After first generating them, our approach for studying these salt “molecules” is to photodetach electrons from their anions. During this past grant cycle, we have extended our

earlier work on salt “molecules” containing singly-charged aluminum cluster anion moieties to those consisting of multiply-charged, aluminum cluster anions. These species are Zintl anions, where the term refers to multiply-charged, polyatomic anions. The multiple negative charges on Zintl anions greatly enhance the stability of ionic and pseudo-ionic lattices. Additionally, due to Coulombic repulsion, multiply-charged clusters are also better protected against agglomeration than are singly-charged clusters. Thus, we expect that multiply-charged aluminum cluster anions will have the potential to be effective building blocks in ionic lattices. Zintl phases are solids or melts composed of Zintl anions and counter-cations, and their occurrence among many metalloids provides precedents for the kinds of aluminum cluster anion-containing salts that we envision. Already, Wang and Boldyrev had shown that several small, multiply-charged aluminum cluster anions, i.e., Al_4^{2-} , Al_4^{4-} , and Al_6^{2-} , are viable by virtue of their aromatic (or anti-aromatic) bonding, and Schweikhard had captured large, bare Al_n^{2-} and Al_n^{3-} cluster anions in a Penning trap.

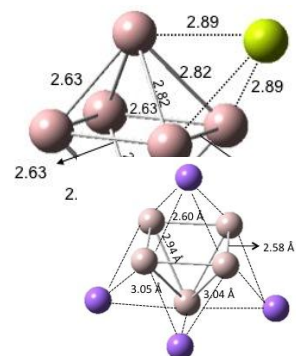
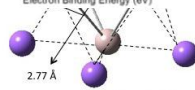
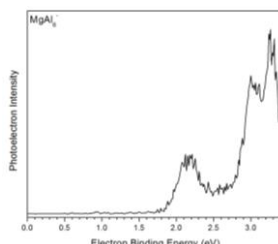
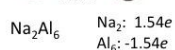
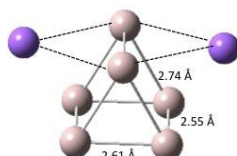
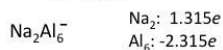
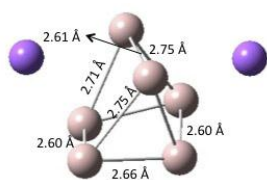
In our work, we generated and photodetached a wide variety of sodium-aluminum cluster anions with an emphasis on systems with multiple sodium atoms in order to provide several electrons to the aluminum moieties. The photoelectron spectra that we measured included those of NaAl_n^- ($n=2-22$), Na_2Al_n^- ($n=2-15$), Na_3Al_n^- ($n=2-14$), Na_4Al_n^- ($n=4-7$), Na_5Al_n^- ($n=6,7$), and Na_6Al_n^- ($n=6-7$). In particular, we have completed an in-depth study of the Zintl characteristics of Na_2Al_6^- and Na_4Al_5^- . Since photodetachment involves not only anions, but also their neutral counterparts, our theoretical collaborators (Jena Kandalam and Kiran) have done calculations on both, i.e., on $(\text{Na}_2\text{Al}_6)^-$ as well as (Na_2Al_6) and on $(\text{Na}_4\text{Al}_5)^-$ as well as (Na_4Al_5) . In each of these two stoichiometries, there exists a 20 valence electron, closed shell, aluminum moiety within either its cluster anion or its corresponding neutral cluster. In addition to determining geometric

structures, where the sodium atoms are found to be outside of the aluminum cages, and computing photodetachment transition energies, which were seen to match the measured values, a full charge analysis of all four species was conducted, thereby illuminating the actual degree of Zintl character in each aluminum moiety (see accompanying figures). While the extent of multiple charging on the aluminum moieties is less, in each case, than that which would have occurred due to full charge transfer from the sodium atoms, it is nevertheless clear that most of aluminum cluster moieties are multiply-charged, Zintl anions and that salts are formed.



Magnesium-Aluminum Clusters

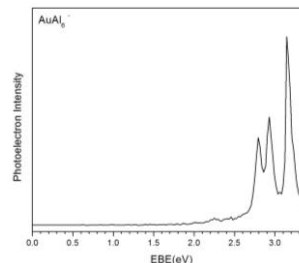
The combination of magnesium and aluminum is



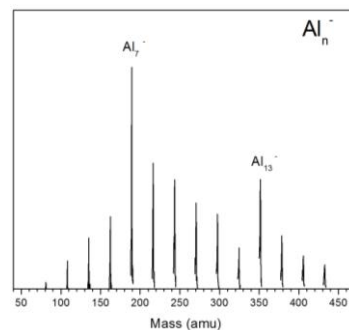
also appealing for propulsion applications. Both are light metals which release copious quantities of energy upon being oxidized. Among the Mg_nAl_m^- photoelectron spectra that we measured thus far, we have focused on those where either the cluster anion or its corresponding neutral cluster has 20 or 40 valence electrons available to it, eg., MgAl_6^- , Mg_2Al_5^- , $\text{Mg}_2\text{Al}_{12}^-$, and $\text{Mg}_3\text{Al}_{11}^-$. Because magnesium is significantly less electropositive and has a higher ionization potential than the alkali metals, it was not initially clear whether these clusters would form ionic systems with

the magnesium atoms outside of an aluminum cage. Our joint work with Jena and his colleagues showed that magnesium often prefers to sit outside of an aluminum cage in MgAl_6^- .

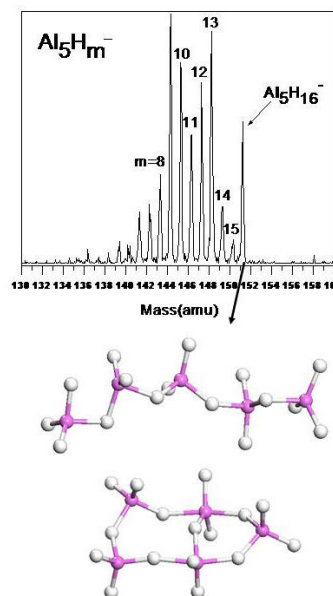
Gold-Aluminum Clusters We have also studied aluminum-gold clusters, where gold is a considerably less electropositive metal than either the alkali or the alkaline earth metals. Together with Gantefoer, we have measured the photoelectron spectra of AuAl_m^- ($m=1-16$), Au_2Al_m^- ($m=1-10$), Au_3Al^- , and Au_4Al^- . Our first paper on this topic will focus on AuAl_6^- and AuAl_7^- . It and another paper on XAl_{13}^- , where $\text{X}=\text{Au}$, Na , and H are joint projects between Jena et al., Gantefoer, and ourselves.



Definitive Confirmation of Aluminum Monovalency in Al_7^- Through an analysis of his photoelectron spectra, Wang showed that aluminum remains monovalent in small Al_n^- clusters up through $n\sim 8$, where s-p mixing (hybridization) becomes strong. Based on his calculations, Jena predicted that Al_7^- is monovalent in some situations and trivalent in others. Castleman proposed that Al_7^- is a super-atom capable of exhibiting multiple valences, depending on its chemical environment. Despite all of this evidence, however, the clear observation of Al_7^- as a magic species in Al_n^- mass spectra has been elusive. We have found definitive mass spectral confirmation that Al_7^- is magic and thus that aluminum can be monovalent in this cluster size range. Our observations were made during PACIS source experiments with magnesium and aluminum and also during experiments with lithium and aluminum. The accompanying mass spectrum has had its Mg_nAl_m^- peaks removed for clearer presentation. We also saw evidence for magic behavior involving Al_7H_n^- in annealing experiments (see below).



Aluminum Hydride Polymers During our continuing investigations of aluminum hydride clusters/molecules, we found evidence for the formation of linear chain and double ring polymeric structures among aluminum hydrides. Under special source conditions, some aluminum hydride cluster anions formed with greater than the usual 3:1 hydrogen-to-aluminum ratio. We conducted experimental and theoretical studies on $\text{Al}_n\text{H}_{3n+1}^-$ anions, where $n=4-8$. Based on a combination of intuitive arguments and calculations, we concluded that these are polymers of aluminum hydrides. The accompanying figure shows the calculated polymeric structures of $\text{Al}_5\text{H}_{16}^-$ and the mass spectrum that provided the first clue to its unusual structure.

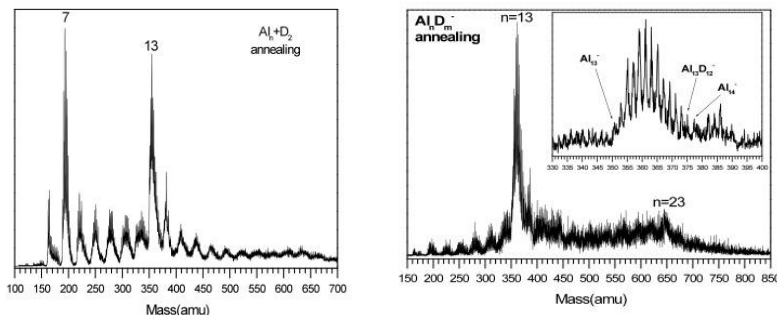


Hydrogen Atom Site-Selectivity and the Shell Model We explored the influence of the shell model on H-atom site-selectivity, using Al_{13}H^- as our main example. Photoelectron spectroscopy revealed that Al_{13}H^- has two isomers and for both provided vertical detachment energies (VDE) for their anions and adiabatic electron affinities (EA_a) for their corresponding neutrals. Theoretical calculations yielded structures of these isomers that differ by the position of the hydrogen atom; in one isomer the hydrogen atom is radially bonded while in the other hydrogen caps a triangular face. The relative energies for both isomers in their anionic and their neutral charge states as well as EA_a and VDE values for both isomers were also calculated. Comparison of calculated and measured detachment energies reconciled the spectrum of each isomer with its structure. Shell model, electron counting considerations correctly predicted the relative stabilities of the anionic isomers as well as those of the neutral isomers.

Aluminum-Based, Magic Number, Mass Distributions among Aluminum Hydrides

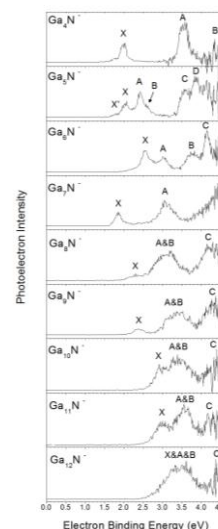
Pulsed arc discharge sources generate intense beams of aluminum hydride cluster anions. But when a second pulsed discharge is added near the exit of its flow tube, the effect is to anneal the anions passing through it,

yielding some extraordinary mass distributions. In particular, annealing results in magic number-like intensity patterns for Al_7H_m^- , $\text{Al}_{13}\text{H}_m^-$, and $\text{Al}_{23}\text{H}_m^-$.



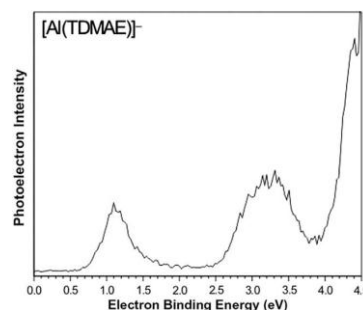
Interestingly, it is not the bare Al_n^- species, [viz. Al_7^- , Al_{13}^- , and Al_{23}^- with magic numbers at 7, 40, and 70 valence electrons, respectively], that are that are especially intense in these mass spectra, but rather their associated hydride distributions. Since each of these distribution islands can be made to dominate by tuning source conditions, it should be possible to use the resultant cluster anion beam directly (without intensity-attenuating mass selection) in additional experiments, eg., deposition.

Gallium Nitride Cluster Anions Because gallium is closely related to aluminum, we also studied a series of Ga_nN_m^- cluster anions, taking the anion photoelectron spectra of Ga_nN^- ($n=4-12$) and Ga_nN_2^- ($n=7-12$). Calculations by Boldyrev and coworkers found structural similarities with aluminum mononitrides in most but not all gallium mononitride cases. We were also able to generate and take photoelectron spectra of gallium dinitride anions. These species were unexpected owing to the strong bond in N_2 and

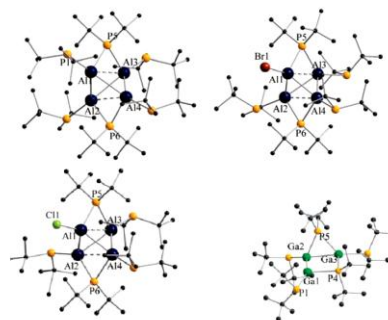


thus the presumed tendency of multiple nitrogen not to bind to gallium. Their structures were also calculated.

Reactivity Studies The reactivity of Al_n^- cluster anions with various reactants goes to the issue of their stabilities in different chemical environments. Building on our earlier, FT-ICR-based reactivity studies between aluminum cluster anions and the gases, O_2 , HCl , Cl_2 , and O_3 , we have extended these studies to beam-flow cell studies. In particular, we have focused on studying Al_n^- reactivity with ammonia and with tetrakis(dimethylamino)ethylene (TDMAE). These two systems are very different. In the case of ammonia, selective etching of Al_{11}^- and Al_{12}^- was found, with little relatively effect on the other Al_n^- sizes. In the case of TDMAE, however, all Al_n^- clusters were destroyed, resulting in a single product where an aluminum atomic anions had inserted into one of the C-N bonds. In both systems, the combination of mass spectrometry, anion photoelectron spectroscopy, and calculations elucidated the energetics involved in these reactions. The photoelectron spectrum of $[\text{Al}(\text{TDMAE})]^-$ is shown in the accompanying figure.



Macroscopic Synthesis of Al_4R_6 Derivatives of Al_4H_6 Working with our collaborator, H. Schnoeckel in Karlsruhe and making use of his unique co-condensation generator, our team synthesized and structurally characterized several derivatives of the Al_4H_6 , which we had earlier discovered in beam experiments. The x-ray characterized structures of the following four derivatives, $\text{Al}_4(\text{P}'\text{Bu}_2)_6$, $\text{Al}_4(\text{P}'\text{Bu}_2)_5\text{Br}$, $\text{Al}_4(\text{P}'\text{Bu}_2)_5\text{Cl}$, and $\text{Ga}_3(\text{P}'\text{Bu}_2)_5$ prepared in this study are shown in the inset figure. This method promises to provide



a pathway for the synthesis of a variety of low oxidation state aluminum and gallium compounds. We have recently constructed a copy of Schnoeckel's co-condensation generator in our lab.